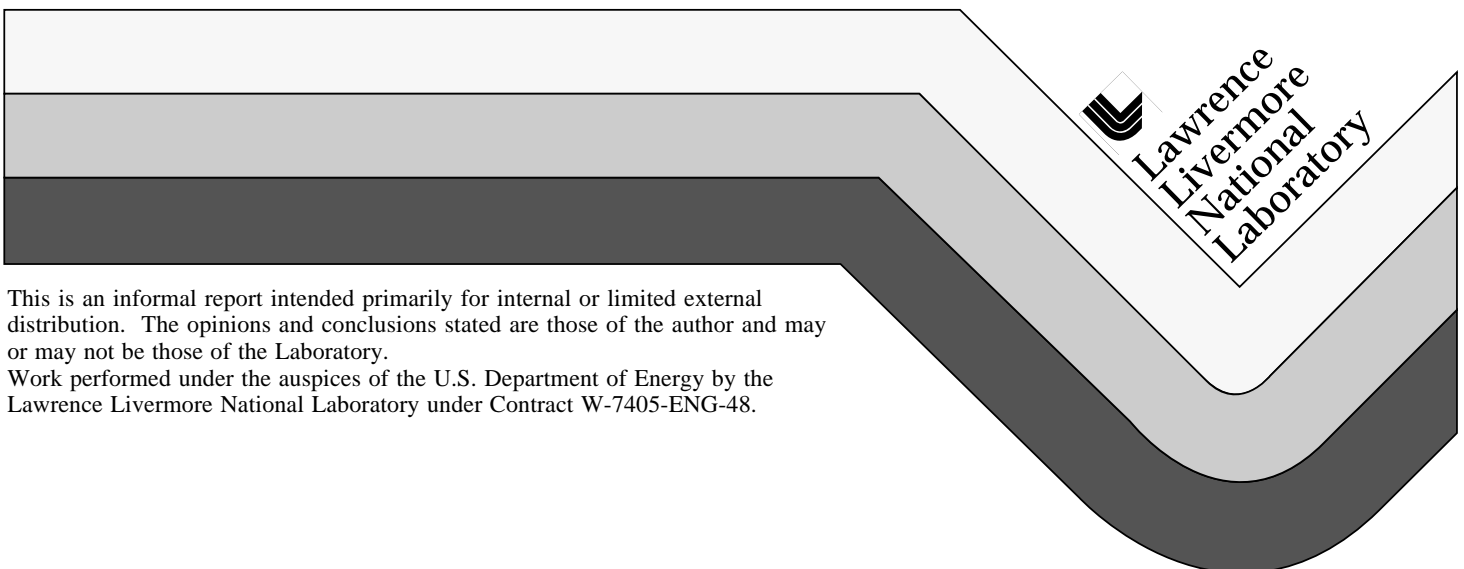


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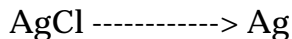
I. Introduction

Mediated Electrochemical Oxidation (MEO) is a non-thermal, aqueous process that treats mixed wastes by oxidizing the organic components of the waste into carbon dioxide and water via chemically active metallic ions (mediators). The MEO process is ideally suited for treating liquid and aqueous mixed wastes. For chlorinated organic wastes, the chlorine will bind with mediator (silver) in the solution to form an insoluble silver chloride. The silver chloride is then separated from the MEO primary system by centrifugation. Replenishment of silver ions into the MEO system is also required to ensure destruction efficiency of MEO process. Since silver is a land-ban metal and it is fairly expensive, an efficient recovery process which converts silver chloride into silver nitrate is required. The integration of the silver recovery into the MEO process would avoid the costly silver make-up to the MEO system and also minimized the discharge of silver to the environment.

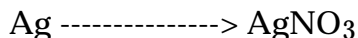
II. Process Selection

It is desirable that the silver recovery method used in MEO be low temperature and aqueous to prevent volatilization of radionuclides. A desirable process should also have high conversion efficiency, not add appreciably to the waste stream, and be economical. In general, there are two steps in all of the aqueous conversion processes we considered for implementation in the MEO System:

- (a) Reduction of AgCl



- (b) Dissolution of Ag



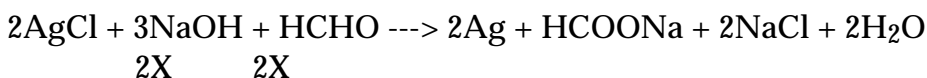
Step (b) is fairly straightforward, the resulting solution AgNO₃/HNO₃ will be sent back to the MEO primary system for reuse. Step (a), however, can be accomplished by a number of methods which were considered and are reviewed below. In general, all of the aqueous recovery methods, except for the method selected for MEO, have undesirable features such as adding organics or toxic metals to the waste stream or involve hazardous reagents.

Review of Aqueous Silver Chloride Reduction Methods

There are many methods available in literature. Here is a brief review of these methods.

(1) Formaldehyde Method

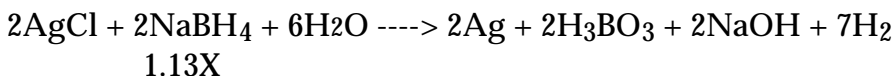
Formaldehyde and sodium hydroxide are required for this method. The reaction is shown as follows:



100% excess of sodium hydroxide and formaldehyde is used for the reduction, consequently, secondary wastes, such as HCHO, HCOONa, and NaCl are problematic.

(2) Sodium Borohydride Method

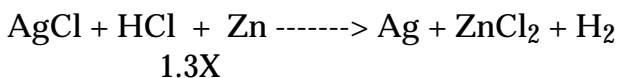
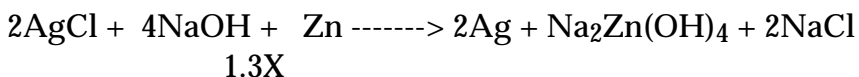
Sodium borohydride is used to reduce silver chloride to silver. A vigorous reaction takes place with hydrogen evolution. The reaction is shown below:

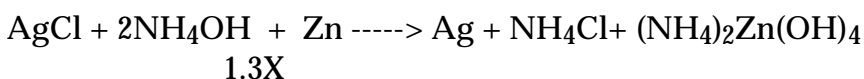


The problems with this method are residual sodium borohydride (due to the 13% excess), product boric acid and the rigorous release of hydrogen. In addition, if not carefully stored and handled, Sodium borohydride can be a fire hazard.

(3) Zinc Method

Zinc powder is a good reducing agent in the presence of liquid media sodium hydroxide, hydrochloric acid, or ammonia. The reactions are shown in the following, respectively:

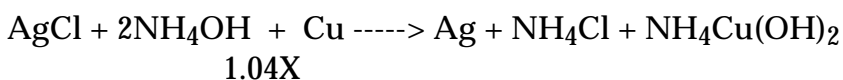




The main problem with the zinc method is the presence of residual zinc and zinc compounds which are LDR.

(4) Copper Method

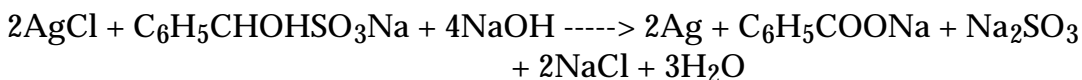
Silver chloride is dissolved in ammonia and can be reduced to silver by copper powder as shown below.



Copper and copper compound are the problem as they are LDR.

(5) Benzaldehyde Method

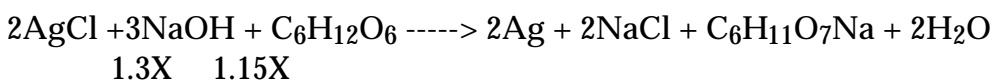
Benzaldehyde can reduce silver chloride to silver in the presence of sodium hydroxide.



The problems with this method are organic wastes and sodium sulfite Na_2SO_3 .

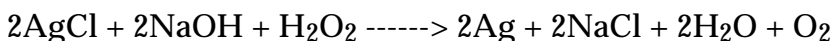
(6) Dextrose Method

Dextrose reduces silver chloride very effectively in the sodium hydroxide solution. However, residual organic wastes are undesirable.



(7) Hydrogen Peroxide Method (Selected Method)

Hydrogen peroxide is a reducing agent in alkaline solutions. It reduces silver chloride into metallic silver. The reaction is shown as follows:



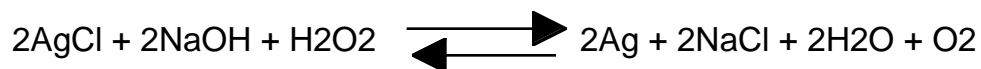
The advantages of this method are: 1. chemicals are inexpensive, 2. no exotic waste will be generated except sodium chloride, waste generation should be very small if low stoichiometry of NaOH is used. Despite its advantages, there is no quantitative information available in the literature. Therefore a lab-scale experiment was initiated to study this process.

III. Experiments

1. Chemical Reactions

Silver chloride is reduced to metallic silver in alkaline solution by hydrogen peroxide. Silver is then separated from the solution, dissolved in nitric acid, and converted into silver nitrate.

Reaction 1



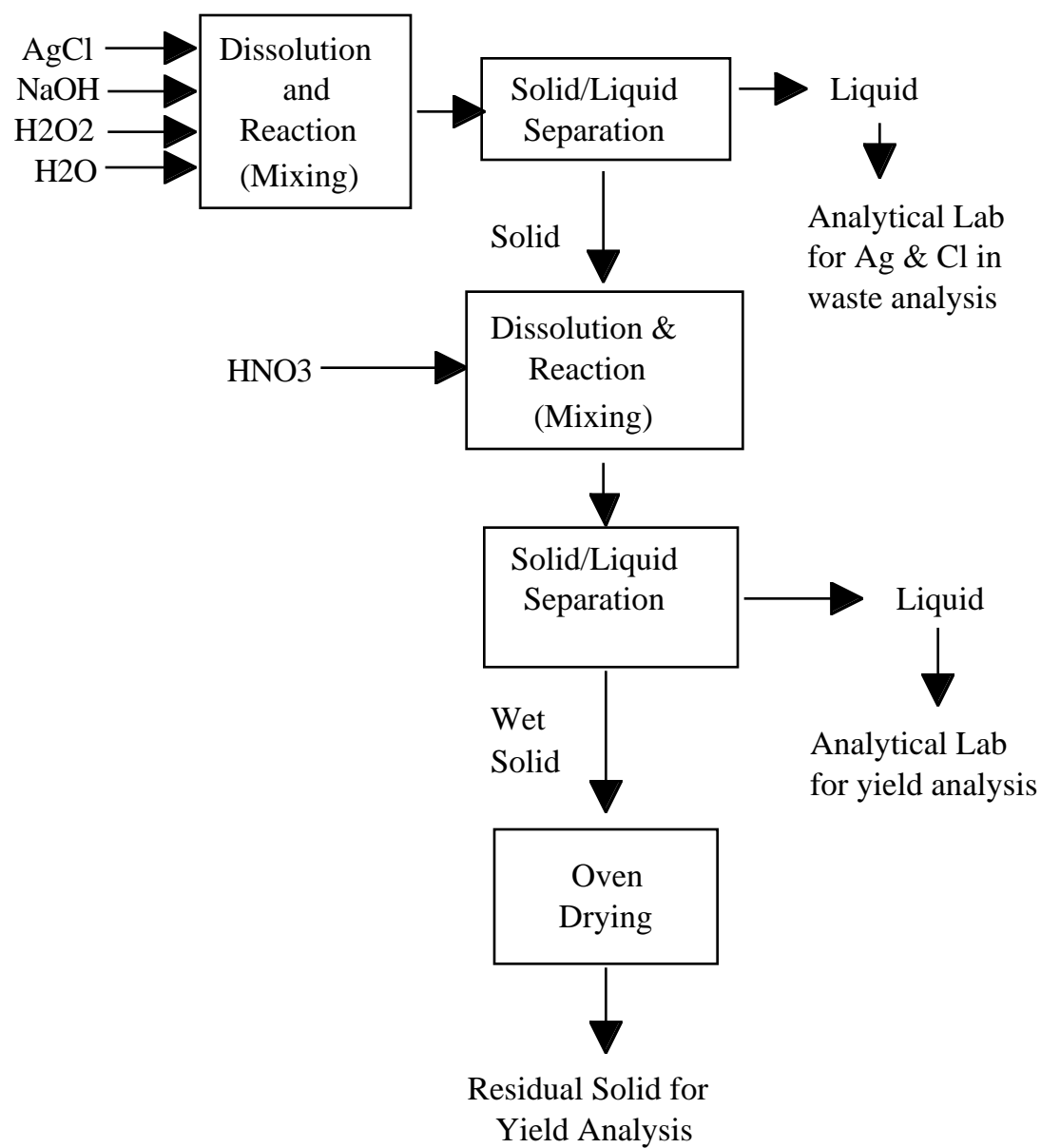
Reaction 2



2. Procedures

The procedures of the lab-scale experiments are shown in the Figure 1, Process Flow Diagram. Silver chloride was added into a solution of sodium hydroxide with mixing at 450 rpm. A heating plate was used to heat the solution to desirable temperatures. The solids turned to dark brown color, an indication of the formation of silver oxide. Hydrogen peroxide was then slowly added to the solution. Rigorous reaction occurred with foaming due to the release of oxygen. After the experimentally varied reaction time was reached, mixing was stopped. The solution was then sent to a filtering funnel or a centrifuge for solid/liquid separation. The liquid was analyzed for silver ions and chlorides. The solids which were metallic silver and unconverted silver chloride were then dissolved into nitric acid at 70 degrees C under magnetic stirring for about 20 minutes. Unconverted silver chloride is insoluble in nitric acid and was filtered out and dried in an oven at 80 degrees. C over night. The conversion efficiency (yield) was calculated based on the amounts of starting and residual silver chloride.

2. Process Flow Diagram (Fig. 1)



$$\text{Conversion Efficiency (Yield)} = (1 - \text{Residual AgCl Solid Out/AgCl into the Process})$$

IV. Results

1. Conversion Efficiencies Vs. Stoichiometries of NaOH & H₂O₂

Based on reaction (1), there are two ways to improve conversion efficiency theoretically, large amounts of NaOH or large amounts of H₂O₂. Both would shift the reaction equilibrium to the right hand side, consequently higher yield could be achieved.

Fig. 2 shows the conversion efficiencies at different NaOH stoichiometries. This curve indicates conversion efficiency is good at high stoichiometries such as 20, but it will generate large amounts of secondary waste salt which is a product of the neutralization of the resulting alkaline solution. With external heating at 80 degrees C, high efficiency can be achieved at stoichiometry of 10 which is still high waste salt. The desirable NaOH stoichiometry is less than 2 to minimize the generation of additional waste. Stoichiometry of 1.25 with external heating was used. The conversion is about 80% which was not too bad, but it did not meet the goal, 90%. Therefore we decided to keep NaOH stoichiometry at 1.25 and change the stoichiometry of H₂O₂.

Fig. 3 shows the effect of H₂O₂ stoichiometry on the conversion efficiency. It indicates that at 1.25X NaOH stoichiometry with external heating at 80 degrees C, 98% conversion is achievable at 10.32X H₂O₂ stoichiometry. The excess H₂O₂ is unstable and breaks down into water and oxygen, which are not undesirable additions to the waste stream.

Hence this is the optimal condition:

NaOH stoichiometry: 1.25X
H₂O₂ stoichiometry: 10.32X

2. Conversion Efficiencies vs. Reaction Time

Since hydrogen peroxide decomposes quickly in alkaline solutions at high temperatures, it will have a negative effect on the conversion due to the back reaction.

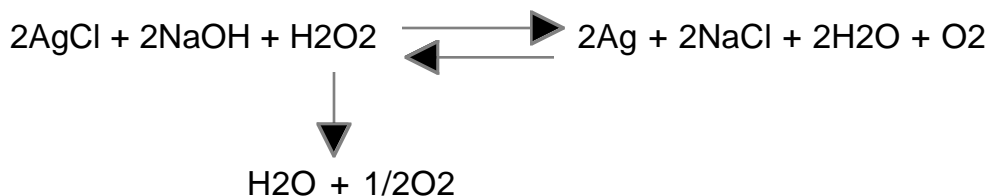


Fig. 4 shows the effect of reaction time on the conversion. The conversion efficiency decreases as the reaction time increases. Therefore, a careful control of reaction time is required.

3. Solution Reuse Study

To minimize the discharge of waste water, reusing solution of reaction 1 may be desirable. This would have the affect of increasing the salt concentration in the waste water, but minimizing the volume of waste water. The purpose of the solution reuse study is to determine: (1) whether the solution is reusable?, and (2) concentrations of silver ions in the waste water, which are LDR and thus would be undesirable to add to the waste stream.

Fig. 5 shows that the solution can be reused several times under the optimal condition without any loss of conversion efficiency.

Fig. 6 indicates that the silver concentrations in the solution increase with increasing salt concentration as expected, but is still very low.

4. Conversion Efficiencies without External Heating

Table 1 shows the conversion efficiencies at optimal condition with and without external heating. The conversions are nearly identical. It indicates that the external heating is not required, and as a result, it will save utility cost for the pilot plant operation.

Table 1

<u>Conditions</u>	<u>Heating</u>	<u>Conversions</u>
1.25X NaOH 10.32X H ₂ O ₂	80 deg C, 15 min.	98.8%
Same	No heating	98.1%

5. Equipment Sizing for Pilot Plant Silver Recovery System

(1) AgCl Dissolver Kettle

At the optimal condition, the amounts & volumes of reagents used for the study are listed in Table 2

Table 2

	<u>AgCl, g</u>	<u>NaOH. Volumes</u>	<u>13N HNO₃ Volume</u>
Lab Scale	28.6	0.185 L	30 CC
Pilot Plant	12,500	81 L	13 L

(2) H₂O₂ Feed Pump

To avoid excess foaming, the H_2O_2 feed rate must be controlled carefully. Table 3 shows that a 2.6 L/min. metering pump is required for the pilot plant.

Table 3

	<u>AgCl, g</u>	<u>H_2O_2 Feed Rates</u>
Lab Scale	28.6	6 cc/min.
Pilot Plant	12,500	2.6 L/min.

6. Regents Needed and Secondary Waste Generation

One of the most important goals for the silver recovery process is to minimize the generation of secondary waste (NaCl). Table 4 shows the amounts of secondary waste generated at the optimal condition is 1.62 kg NaCl per kg of chlorinated organic fed to MEO, assuming the excess NaOH is neutralized with HCl.

Table 4

<u>MEO Feed</u> *	<u>AgCl</u>		<u>NaOH</u> <u>H_2O_2</u>	<u>NaCl Generated</u>		
kgmol kg	kgmol	kgmol L	kg	(50%) kg/kg		
1	62	1.37	1.71	411	100	1.62

* Halogenated Wastes per Ref. 1

V. Conclusions

1. An efficient process has been developed in the lab-scale to convert silver chloride into silver nitrate. The conversion efficiency is better than 90%.
2. The process is non-toxic, low temperature, and does not involve the use of hazardous reagents.
3. The process is economical. The reagents required are sodium hydroxide and hydrogen peroxide which are inexpensive.
4. Generation of secondary waste is small due to the low stoichiometry of NaOH used for the conversion.

References

1. "Mixed Waste Management Facility- Conceptual Design Report", UCRL-Prop-11676, L-17293, 1994
2. "Recovery of Silver from and Some Uses for Waste Silver Chloride", J.A. Murphy, A.H. Ackerman, and J.K. Heeren, J. Chem. Ed., 68(7), p.602, 1991.
3. "Process for Making a Silver Nitrate Solution", L. Rosato, M. Blais, European Patent Application, EP 0 568 259 A1, 1993.

**Fig. 2 Conversion of AgCl into AgNO₃
at various NaOH Stoichiometries**

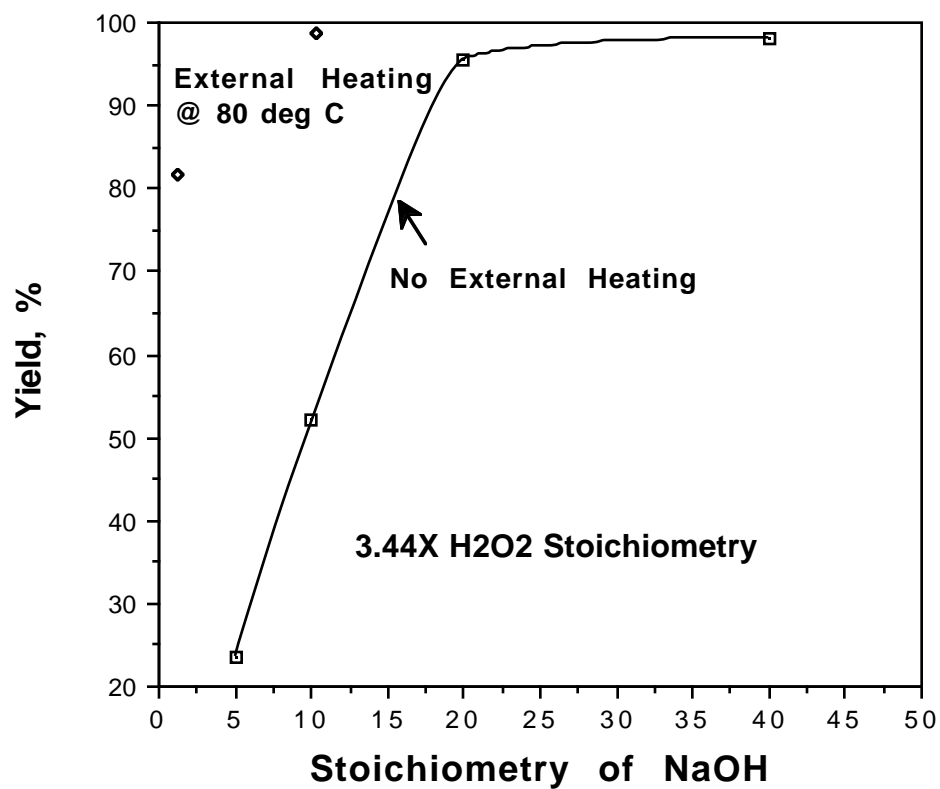


Fig. 3 Effect of H₂O₂ Stoichiometry on Conversion Efficiency

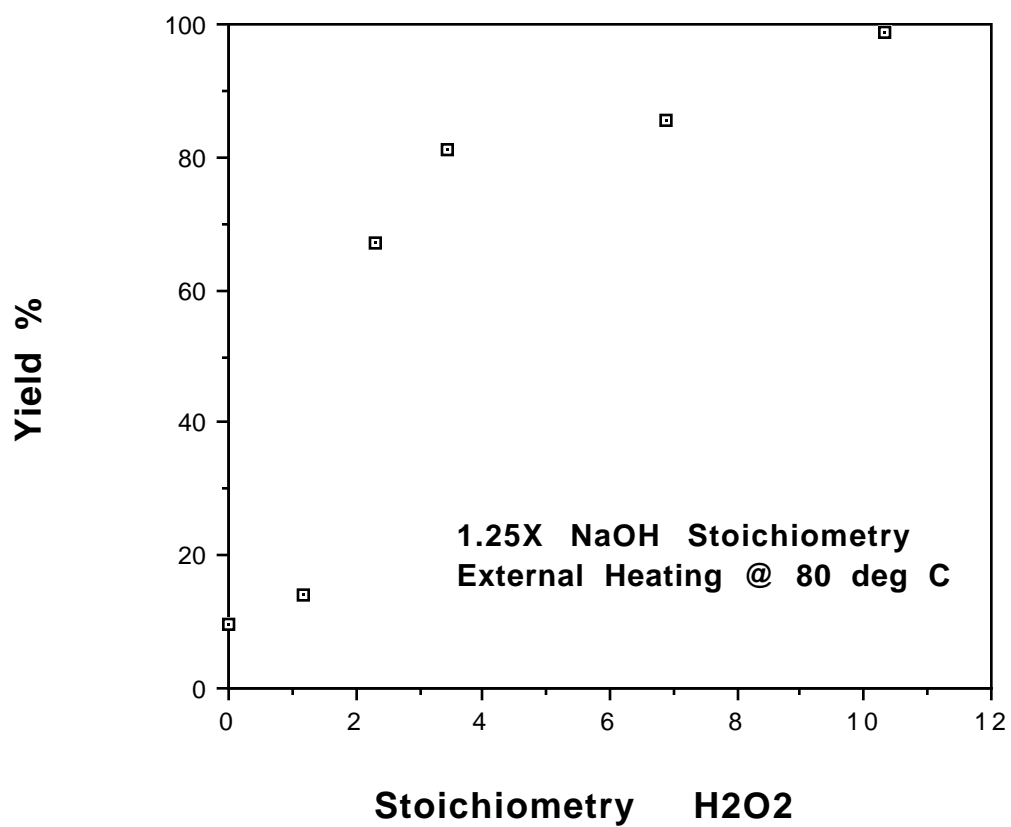


Fig. 4 Conversion Vs. Reaction Time

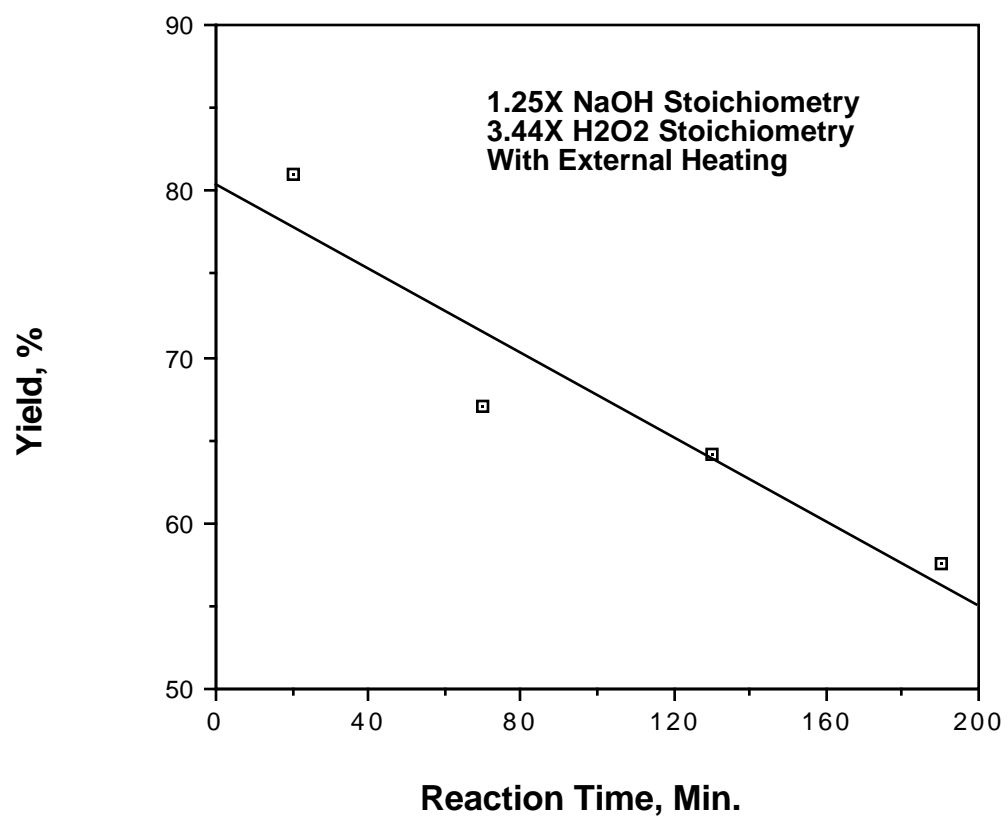


Fig. 5 Solution Reuse Study

Conversion of AgCl to AgNO₃

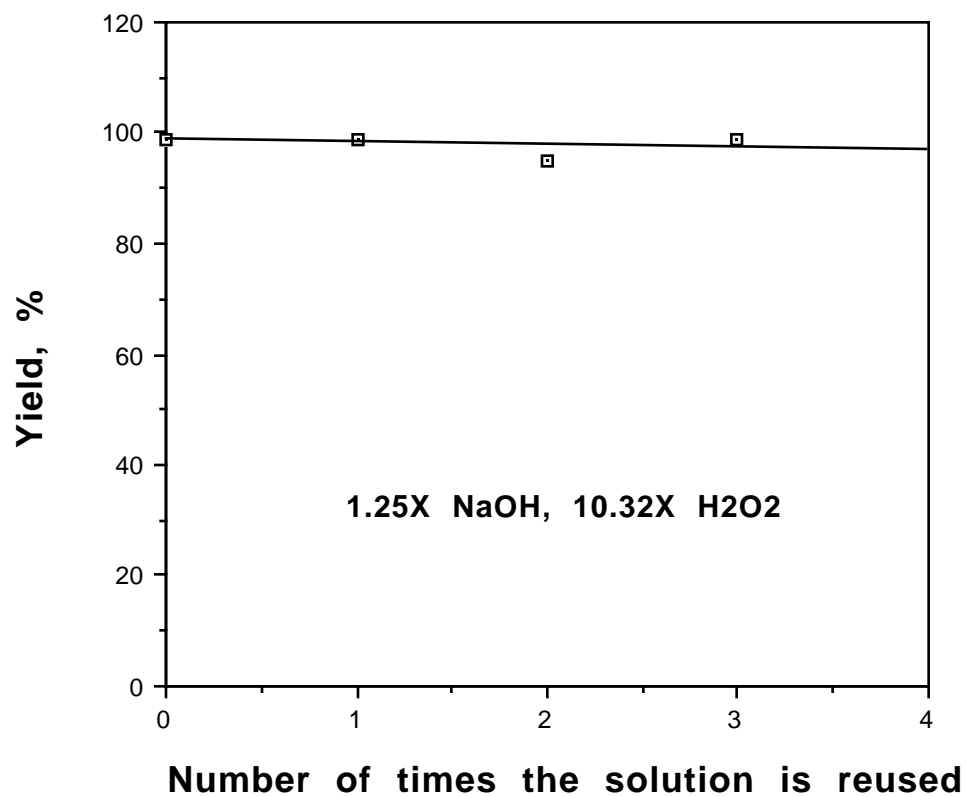


Fig. 6 Ag to salt ratio in the waste water
as a function of the number of times the
solution is reused

